# Influence of Charge Doping on Thermal Diffusivity of Double Perovskite Sr$_2$FeMoO$_6$ Studied by Mirage Effect [1]

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**ABSTRACT**

Effects of charge doping on thermal diffusivity have been investigated in double perovskite ferromagnetic Sr$_{2-x}$La$_x$FeMoO$_6$ ($0.0 \leq x \leq 0.4$) by means of mirage effect at 300 K ($<<$ the critical temperature $T$c ~ 420 K). Substitution of the La$^{3+}$ ions for the Sr$^{2+}$ ions significantly increases the value of thermal diffusivity from 0.39 cm$^2$/s at $x = 0.0$ to 0.54 cm$^2$/s at $x = 0.4$. The larger thermal diffusivity has been ascribed to the extra itinerant electrons on the Mo4$d_{\downarrow}$ band.

**KEYWORDS:** Charge doping; Double perovskite; Thermal diffusivity; Mirage effect

## 1. INTRODUCTION

Carrier doping in strongly correlated electron systems is a powerful tool to discover the new phenomena and synthesize the new materials. High-$T$c superconducting cuprates and pervoskite-structural manganites are the most celebrated examples. In the latter case, the parent complex LaMnO$_3$ is insulating and antiferromagnetic. A metallic and ferromagnetic behavior is promoted with substitution of the divalent Sr$^{2+}$ ions for the trivalent La$^{3+}$ ions. The generic features of magnetic and transport properties of this system are well understood in the framework of double exchange (DE) mechanism, which includes the transfer of the $e_g$ electrons (transfer integral $t$) and the strong Hund's rule coupling $J$ between the local $t_{2g}$ spins and the $e_g$ electrons [1].

Recently, transition metal oxides with ordered double-perovskite structure, $A_2M$MoO$_6$, $A_2M$ReO$_6$ and $A_2M$WO$_6$, ($A$ is rare-earth metal and $M$ is transition metal) currently attract considerable interest from the viewpoint of fundamental physics and technological applications to magnetoresistance devices [2-3]. Among them, $A_2$FeMoO$_6$ ($A$= Ca, Sr, and Ba) is known to be ferromagnetic with a critical

temperature $T$c (= 330 ~ 420 K) [3], which is higher than that of charge doped manganites, e.g., $T$c ~360 K for $La_{0.6}Sr_{0.4}MnO_3$. In this system, $Fe^{3+}$ ions ($3d^5$) behave as local spins, while the conduction band is occupied by the $4d$ electrons of $Mo^{5+}$ ($4d^1$) ions [4]. Navarro *et al.* [5] investigated the effects of the electron doping on the magnetic and structural properties in $Sr_2FeMoO_6$, and found a substantial reduction of the saturation magnetization $M_s$. They have ascribed the reduced $M_s$ to the increased antisite disorder of the Fe and Mo ions due to substitution of $La^{3+}$ ions for $Sr^{2+}$ ions. Moritomo *et al.* [6] also observed the same behavior in the same system. By contrast, they interpreted the observed behavior in terms of the occupation of the doped electrons in the down-spin Mo4$d$ band. On the other hand, from the viewpoint of thermal dynamics, the thermal diffusivity should be increased by the extra itinerant electrons in the Mo4$d$ band, and decreased by the antisite disorder of the Fe and Mo ions. Therefore, investigation of the thermal properties may be a key to clarify the origin of the reduced saturation magnetization $M_s$. However, little study has been made on the thermal properties, *i.e.*, thermal diffusivity and thermal conductivity of the double-perovskite system, especially for the influence of electron doping on the thermal properties.

The photoacoustic (PA) and photothermal (PT) techniques have been successfully applied to characterize the thermal properties of solids in the last decade [7]. In this paper, we measured the thermal diffusivity of the electron doped double perovskite-type $Sr_{2-x}La_xFeMoO_6$ ($0.0 \leq x \leq 0.4$) by means of the mirage effect at 300 K. The thermal diffusivity shows a gradual increase with increasing the La doping concentration $x$, suggesting that the doped electrons occupy mainly the down-spin Mo4$d$ band.

## 2. EXPERIMENT

The melt-grown crystals, $Sr_{2-x}La_xFeMoO_6$ ($0.0 \leq x \leq 0.4$), were made by the floating-zone method [5]. A stoichiometric mixture of commercial $SrCO_3$, $La_2O_3$, $Fe_2O_3$, Mo, and $MoO_3$ was well ground, and pressed into a rod with a size of φ 5mm×

100mm and sintered at 1200℃ for 2h in a flow of Ar gas. The crystal was grown at a feeding speed of ~20 mm/h in the Ar atmosphere. Black and shiny crystals, typically 4-5 mm in diameter and ~20 mm in length, were obtained. X-ray diffraction (XRD) measurement and Rietveld analysis of the patterns indicate that the obtained crystals have a tetragonal (I4/mmm; $Z = 2$) symmetry, consistently with the previous reports [2-3]. The antisite disordering of the Fe and Mo ions was estimated around 15 % in $x = 0$, and increased to 17 % with increasing $x$ to 0.4.

In the mirage effect [7], the thermal diffusivity is measured by searching the zero-crossing points of the in-phase component of the transverse mirage-effect deflection signal, which is used to determine the thermal wavelength. The distance $x_0$

between the two zero crossing points on both sides of the origin is given by

$$x_0 = d_0 + (\pi\alpha/f)^{1/2}, \tag{1}$$

where $d_0$ is a distance on the order of the heating-beam diameter, $f$ is the modulation frequency and $\alpha$ is the thermal diffusivity of the sample. Thus, a plot of $x_0$ vs the reciprocal of the square root of the frequency should have a slope given by $(\pi\alpha)^{1/2}$. The modulation-frequency range in the experiments was usually from 100 Hz to 4 kHz [8].

## 3. RESULTS AND DISCUSSION

Before describing details of the influence of electron doping on the thermal properties for $Sr_2FeMoO_6$, let us survey the variation of the magnetic and structural properties with substitution of $La^{3+}$ for $Sr^{2+}$ ions. Figure 1 shows the magnetization curves for $Sr_{2-x}La_xFeMoO_6$ crystals at 50 K. The magnetization $M$ rapidly increases with external magnetic field $H$, and then saturated when $H$ reaches to 4 T. The saturation magnetization $M_s$ decreases with $x$ increasing: $M_s = 3.3\ \mu_B$ at $x = 0.0$ and $M_s = 2.4\ \mu_B$ at $x = 0.4$. Such a result is consistent with the previous works carried out by Navarro $et\ al$. [5] and Moritomo $et\ al$. [6].
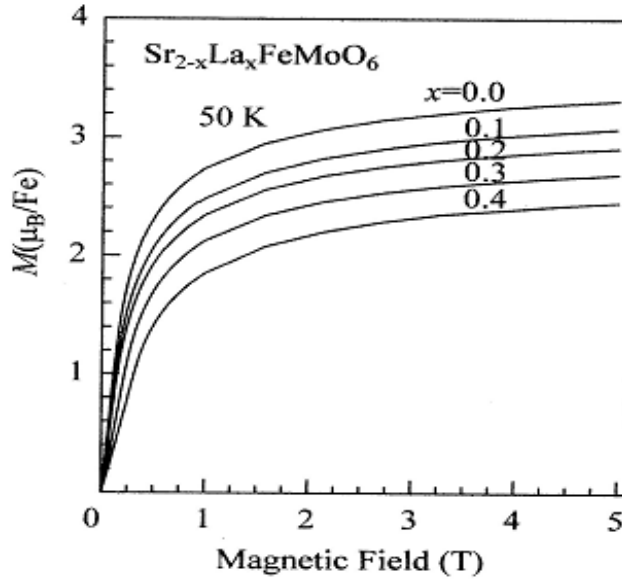


**Fig.1.** Magnetization curves at 50 K for $Sr_{2-x}La_xFeMoO_6$ ($0.0 \le x \le 0.4$), which was measured after cooling down to 50 K in zero field (ZFC).

Figure 2 shows the x-ray diffraction (XRD) powder patterns of the $Sr_{2-x}La_xFeMoO_6$ at 300 K: the upper and bottom panels are for $x=0.1$ and 0.4, respectively. It shows that the samples have a small amount of $SrMoO_4$ impurity phase, in accordance with previous reports [2, 3]. In both compounds, all XRD peaks except for the peaks of $SrMoO_4$ can be indexed according to the space group (I4/mmm; $Z = 2$),

indicating that there is no distinguished structure change with La substitution from $x = 0.0$ to $0.4$.

In order to understand the origin of the suppressed $M_s$ upon La substitution, let us consider the variation of the thermal diffusivity with $x$. We illustrate in Fig. 3 (a) the $x$ dependence of the thermal diffusivity $\alpha$ for $Sr_{2-x}La_xFeMoO_6$ at 300 K. With increase of $x$ from 0.0 to 0.4, the $\alpha$-value gradually increases from 0.39 cm$^2$/s to 0.54 cm$^2$/s. As compared, we plotted the $x$ dependence of the $M_s$-values obtained at 50 K in Fig. 3 (b). We have found that the $x$ dependence of $\alpha$-value has an opposite trend to that of the $M_s$. For magnetic materials, the thermal diffusivity is usually written as a sum of three terms [9], $\alpha = \alpha_{ph}+\alpha_{el}+\alpha_{sp}$, where $\alpha_{ph}$, $\alpha_{el}$ and $\alpha_{sp}$ are the contributions from phonon, electron and spin, respectively. As there is no structural change upon La substitution from $x = 0.0$ to $0.4$, the $\alpha_{ph}$ should be constant. If the spin contribution $\alpha_{sp}$ is dominant, the thermal diffusivity should be decreased by the antisite disordering of the Fe and Mo ions. Therefore, the increase in the thermal diffusivity with La substitution should be attributed to the contribution of the electronic part $\alpha_{el}$, *i.e.*, the occupation of the extra itinerant electrons in the Mo$4d$ band.
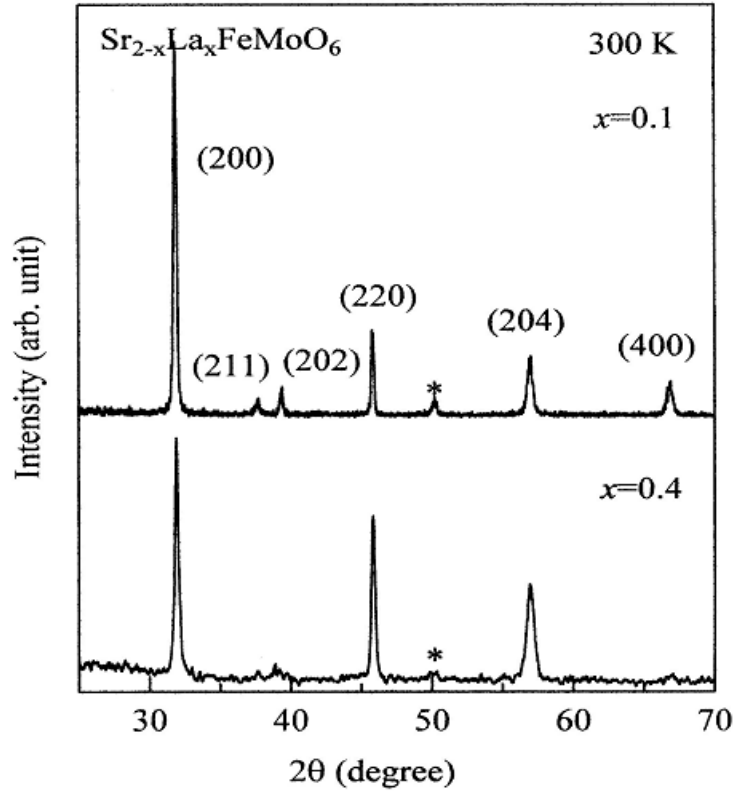


**Fig.2.** XRD patterns of the $Sr_{2-x}La_xFeMoO_6$ at 300 K: the upper and bottom panels are for $x = 0.0$ and 0.4, respectively. The peaks due to impurity $SrMoO_4$ are noted by *.

It has been recently shown that the dominant magnetic interaction in $Sr_2FeMoO_6$ is ferromagnetic, and likely of DE interaction as found in the manganites [10]. Within the DE scenario, the ferromagnetic coupling between the local $Fe^{3+}$ spins is mediated by the Mo4$d$ band near the Fermi level $E_F$. Thus, the $M_s$ should increase with increasing the itinerant electron density in the Mo4$d$ band. However, this picture cannot account for the experiment data, i.e., the reduced $M_s$. (see Fig. 3(b)) The structural analysis also implies the enhanced $M_s$: the Fe-O-Mo bonds are closed upon La substitution and hence larger hopping integral Fe-O-Mo of the itinerant electrons [5]. What is the origin of the suppressed $M_s$? Kanamori *et al.* [11] proposed an alternative model for the magnetism of $Sr_2FeMoO_6$. If the $Fe^{3+}$ spins are ferromagnetically ordered, the hybridization between the Fe3$d$ and Mo4$d$ states pushes up (down) the up-spin Mo4$d_\uparrow$ (down-spin Mo4$d_\downarrow$) states located between the Fe3$d_\uparrow$ and Fe3$d_\downarrow$ levels, as shown in Fig.4. Then, the electrons near $E_F$ level transfer from the Mo4$d_\uparrow$ band to the Mo4$d_\downarrow$ band. Thus, the extra electrons should be doped in the Mo4$d_\downarrow$ band. Since their spins are antiparallel to the local Fe3$d_\uparrow$ spins, the reduced $M_s$ is expected, as observed.



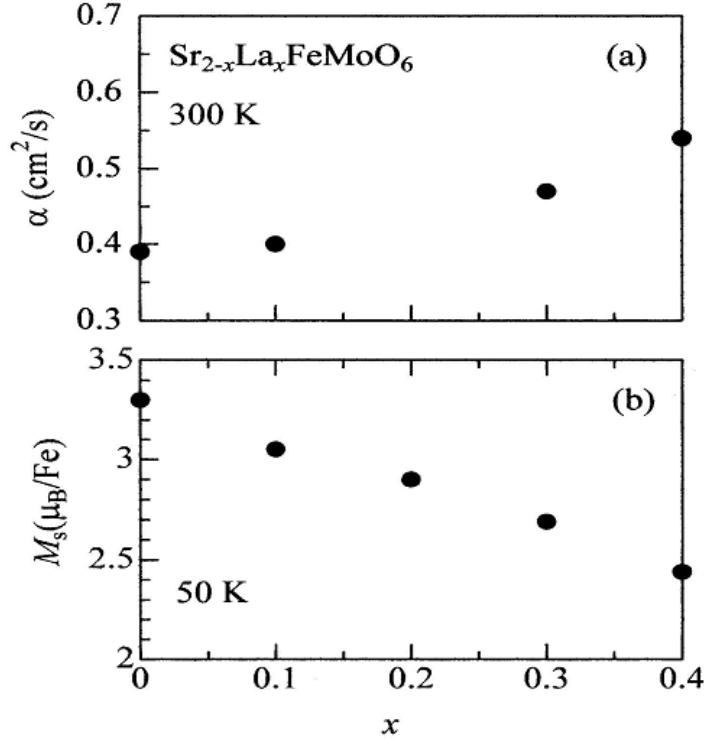**Fig.3.** La concentration $x$ dependence of (a) the thermal diffusivity $\alpha$ at 300 K and (b) the saturation magnetization $M_s$ at 50 K for $Sr_{2-x}La_xFeMoO_6$ ($0.0 \leq x \leq 0.4$).

## 4. SUMMARY

We have investigated the influence of charge doping on the thermal diffusivity in double perovskite $Sr_2FeMoO_6$ by substitution of $La^{3+}$ ions for $Sr^{2+}$ ions. The thermal

diffusivity was found to increase with La concentration, which is ascribed to the occupation of extra itinerant electrons in the down-spin Mo4$d$ band. This result is helpful to clarify the reduced saturation magnetization $M_s$ upon La substitution. Thus, the PA and PT techniques are a powerful tool to investigate the micro-mechanism of the materials.
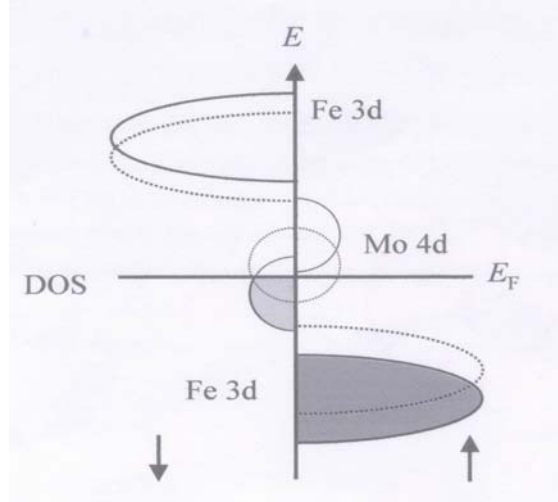


**Fig.4.** Schematics for variation of density of state (DOS) in $Sr_2FeMoO_6$ in ferromagnetic phase: the solid one is proposed by Kanamori and the broken one is normal. ↑ and ↓ represent the up-spin and down-spin states, respectively.

**ACKNOWLEDGMENT**

**REFERENCES**

1. P. W. Anderson and H. Hasegawa, *Phys. Rev.* **100** (1955) 675.
2. K. I. Kobayashi, T. Kimura, H. Sawada, K. Terakura and Y. Tokura, *Nature* **395** (1998) 677.
3. Y. Tomioka, T. Okuda, Y. Okimoti, R. Kumai, K. I. Kobayashi and Y. Tokura, *Phys. Rev. B* **61** (2000) 422.
4. F. Galasso, F. C. Douglas and R. Kasper, *J. Chem. Phys.* **44** (1966) 1672.
5. J. Navarro, C. Frontera, L. Balcells, B. Martinez and J. Fontcuberta, *Phys. Rev. B* **64** (2001) 092411.
6. Y. Moritomo, S. Xu, T. Akimoto, A. Machida, N. Hamada, K. Ohoyama, E. Nishibori, M. Takata and M. Sakata, *Phys. Rev. B* **62** (2000) 14224.
7. P. K. Kuo, M. J. Lin, C. B. Reyes, L. D. Favro, R. L. Thomas, D. S. Kim and S. Y.

Zhang, *Cdn. J. Phys.* **64** (1986) 1165.

8. L. Guo, S. Y. Zhang, X. R. Zhang, J. He and Z. N. Zhang, *Appl. Phys. A* **60** (1995) 395.

9. S. W. Gerth, B. Franz, H. W. Gronert and E. F. Wassermann, *J. Magn. Magn. Mater.* **101** (1991) 37.

10. D. D. Sarma, P. Mahadevan, T. S. Dasgupta, S. Ray and A. Kumar, *Phys. Rev. Lett.* **85** (2000) 2549.

11. J. Kanamori and K. Terakura, *J. Phys. Soc. Jpn.* **70** (2001) 1433.